

## \* NOTICES \*

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to an adhesive composition. It is related with the polyimide system adhesive composition which demonstrates a good adhesive property under a room temperature condition in detail.

[0002]

[Description of the Prior Art]Conventionally, the heat-resistant adhesives which use aromatic polyimide etc. as the main ingredients are used for adhesion between substrate-copper foil in a flexible printed circuit board. However, since aromatic polyimide generally does not dissolve in a general-purpose organic solvent, It is used as a solution of the aromatic polyamic acid which is a precursor of that, imide-ized down stream processing of heating at an elevated temperature for a long time is specifically succeedingly needed for spreading and desiccation of a solution, and there were problems -- generating of a void phenomenon and thermal degradation of the electronic parts themselves are seen in this case.

[0003]On the other hand, although siloxane polyimide of solvent fusibility is indicated by JP,61-118424,A and JP,1-121325,A, If it applies to the problem that heat resistance is low, the problem that the solubility over various organic solvents is not necessarily enough, and a flexible printed circuit board and dries to these advanced technology, the problem that the substrate curls greatly etc. will be seen.

[0004]

[Problem(s) to be Solved by the Invention]Previously, to a general-purpose organic solvent, an applicant is siloxane polyimide of fusibility and as an adhesive composition using this as the main ingredients of the adhesives of the substrate-copper foil indirect arrival of a flexible printed circuit board, The adhesive composition containing solvent soluble siloxane polyimide, the epoxy resin, diamine system hardening agent, and organic solvent which consist of a

copolymer of a diaminopolysiloxane alicycle-like diamine mixture and aromatic tetracarboxylic dianhydride is proposed (Japanese Patent Application No. No. 354,825 [ eight to ]).

[0005]Although the adhesive composition which has such a presentation was excellent in the heat-resistant adhesive property, in respect of the adhesive property under room temperature conditions, it is not necessarily satisfied, and the improvement at the point was newly called for.

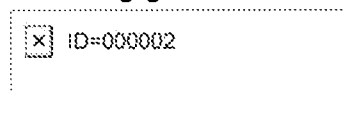
[0006]The purpose of this invention is to provide the thing which made the adhesive property under the room temperature conditions of that improve in the adhesive composition which makes siloxane polyimide of fusibility a general-purpose organic solvent with an adhesive component.

[0007]

[Means for Solving the Problem]The purpose of this this invention is attained by adhesive composition containing siloxane polyimide, an epoxy resin, a diamine system hardening agent, a fluorochemical surfactant, and an organic solvent which consist of a copolymer of a diaminopolysiloxane alicycle-like diamine mixture and aromatic tetracarboxylic dianhydride.

[0008]

[Embodiment of the Invention]As a diaminopolysiloxane which is one ingredient of the diamine compound reacted to aromatic tetracarboxylic dianhydride, the compound expressed with the following general formulas is used.



R: the carbon numbers 2-6 -- desirable -- the integer of the low-grade alkyl group of the divalent hydrocarbon-group  $R_1$ - $R_4$ ; carbon numbers 1-5 of 3-5, and the phenyl group n:0-30 -- desirable -- the integer of 4-12 [0009]As this compound, the compound R and  $R_1$  - whose  $R_4$  are the combination of the following substituents is illustrated.

$\underline{R_1} \underline{R_2} \underline{R_3} \underline{R_4} \cdot (CH_2)_3 CH_3 CH_3 CH_3 CH_3 (CH_2)_4 CH_3 CH_3 CH_3 CH_3 (CH_2)_3 CH_3 C_6 H_5 CH_3 C_6 H_5 p-$   
 $C_6 H_4 CH_3 CH_3 CH_3 CH_3$  [0010]Actually, commercial item, for example, Toshiba Silicone product

TSL, 9386, TSL9346, TSL9306, Toray Industries Dow Corning product BY16-853U, Shin-etsu chemicals X-22-161AS, and Nippon Unicar product F2-053-01 grade can be used.

[0011]As alicycle-like diamine which is a diamine compound of another side, The diamine which generally has one or more cyclohexane rings, for example, 1,3-bis(aminomethyl) cyclohexane, 1,4-bis(aminomethyl)cyclohexane, 1,3-diaminocyclohexane, etc. are independent, or are used as a mixture.

[0012]these diaminopolysiloxanes and alicycle-like diamine -- the former -- about 95-5-mol % -- it is about 80-40-mol% of a rate preferably -- the latter -- about 5-95-mol % -- it is preferably

used at about 20-60-mol% of a rate. If the adhesive composition which was excellent also in the heat-resistant adhesion effect when there were few latter rates than this cannot be obtained but it is used at many rate from this on the other hand, it will become the adhesion presentation which lacks in pliability.

[0013]As aromatic tetracarboxylic dianhydride reacted to these diamine compound mixtures, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 3, 3',4,4'-diphenylsulfone tetracarboxylic dianhydride, 4,4'-oxydi phthalic acid dianhydride, 4, 4'-biphthalic dianhydride, 2,2'-diphthalic-acid-dianhydride propane, diphthalic-acid-dianhydride methane, pyromellitic dianhydride, 2,2'-(hexafluoro isopropylidene) diphthalic acid dianhydride, etc. are used at a rate of equimolar to a diamine compound mixture.

[0014]Although the reaction of a diamine compound mixture and aromatic tetracarboxylic dianhydride is preferably performed in aprotic polar solvents, such as dimethylformamide, dimethylacetamide, and N-methyl pyrrolidone, it is performed also in polar solvents, such as cresol and pyridine. Actually, it is carried out by dropping a diamine compound mixture at about 0-10 \*\* into the polar solvent solution of aromatic tetracarboxylic dianhydride.

[0015]Since this resultant is polyamic acid which is a polyimide precursor, dehydration for polyimide-izing it is performed. Dehydration is preferably performed by making it react at about 100-200 \*\* using dehydrators, such as an acetic anhydride.

[0016]Siloxane polyimide which is the output of a polyimide-ized reaction, For example, when alicycle-like diamine is bis(aminomethyl)cyclohexane, also being considered the block copolymer which has the repeating unit (a) and (b) expressed with the following general formulas -- the weight average molecular weight Mw (measurement by GPC; polystyrene conversion) of that -- about 10000-100000 -- it is about 25000 to about 75000 preferably.

⊗ ID=000003

⊗ ID=000004

It reaches.

Ar: Aromatic tetracarboxylic acid residue [0017]The obtained siloxane polyimide makes an adhesive composition form there by adding an epoxy resin, a diamine system hardening agent, a fluorochemical surfactant, and an organic solvent.

[0018]As an epoxy resin, arbitrary things, such as a bisphenol A type, a biphenyl type, a glycidyl amine type, and a novolac type, etc. are used, and the commercial item 154, 604, and

871, for example, oil recovery shell epoxy product Epicoat, and 828 grades are used actually. These epoxy resins are preferably used at a rate of about 0.1 to 10 weight section about 0.1 to 30 weight section to siloxane polyimide 100 weight section. If there are few using rates of an epoxy resin than this, an adhesive property will come to fall, and if it is used at many rate from this on the other hand, heat resistance will come to fall.

[0019]A diamine system hardening agent is what is used as a hardening agent of an epoxy resin, For example, 4,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenylmethane, m-phenylenediamine, m-xylylene diamine, isophoronediamine, diethylenetriamine, triethylenetetramine, etc. are preferably used at a rate of about 0.1 to 10 weight section about 0.1 to 30 weight section per siloxane polyimide 100 weight section.

[0020]As a fluorochemical surfactant, perfluoro octanoic acid ammonium, Perfluoro aliphatic-carboxylic-acid ammonium, such as perfluoro nonanoic acid ammonium, Perfluoro hexenyloxy sodium benzenesulfonate etc. are used, A thing the PFE type of a commercial item, for example, NEOSU products, a DFE type, and FT type etc. are actually used at a rate of about one to 5 weight section preferably about 0.1 to 10 weight section per siloxane polyimide 100 weight section. In the using rate not more than this, if the adhesive improvement under room temperature conditions is not attained but it is used at a rate beyond this on the other hand, a beautiful film will become as [ obtain / film / carry out phase separation to siloxane polyimide, and ].

[0021]It is made to dissolve in general-purpose low-boiling point organic solvents, such as methyl ethyl ketone, chloroform, a tetrahydrofuran, and toluene, preferably about ten to 50% of the weight with about 20 to 40% of the weight of solids concentration, and each above ingredient makes an adhesive composition solution form there.

[0022]This adhesive composition solution is used effective in adhesion between substrate-copper foil of a flexible printed circuit board, etc. Effective adhesion is performed by applying this solution to flexible base materials, such as a polyimide film, and pasting together the copper foil which constitutes printed wiring there when using it, carrying out for [ about 100 seconds ] grade heating at about 185 \*\*, and also carrying out a cure at about 180 \*\* for about 12 hours.

[0023]

[Effect of the Invention]The adhesives which use as effective adhesion components the new siloxane polyimide provided by this invention, Adhesion spreading conditions mild as fusibility are made possible for the aromatic polyimide which was insolubility even at an aprotic polar solvent also at a general-purpose low-boiling point organic solvent, It not only enables adhesion in low temperature and a short time, but the effect outstanding also in respect of [ under room temperature conditions ] the adhesive property is shown without necessity's carrying out hot and prolonged sticking by pressure like the conventional aromatic polyimide

system adhesives. The phenomenon in which a substrate curls greatly etc. is not seen by the flexible printed circuit board which between substrate-copper foil pasted up effectively using this adhesive composition, either.

[0024]

[Example]Next, this invention is explained about an example.

[0025]To a separable flask with one to example 3 capacity of 100 ml, 1.61g (5 millimol) of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 15 ml of N-methyl pyrrolidone are taught under a nitrogen atmosphere, and the solution is cooled on ice. There,

Diaminopolysiloxane [Toshiba Silicone product TSL9386 which is the specified quantity, respectively; Each of  $_3$  ( $\text{CH}_2$ ) groups,  $\text{R}_1 - \text{R}_4$  R by said general formula  $\text{CH}_3$  group] and 1,3-bis(aminomethyl)cyclohexane. After adding maintaining the temperature of about 0-10 \*\*, it stirred for 30 minutes and was made to dissolve under a room temperature. Then, after carrying out temperature up to 50 \*\* and also stirring for 3 hours, temperature up is carried out to 200 \*\*, it stirred for 3 hours and dehydration was carried out. Siloxane polyimide was obtained by underwater reprecipitation after ending reaction.

[0026]To siloxane polyimide 100 obtained weight section, epoxy resin (Epicoat 604) 1 weight section, 4,4'-diaminodiphenyl sulfone 1 weight section and fluorochemical surfactant (NEOSU product PFE-800B) 1 weight section were added, and it prepared as a methyl-ethyl-ketone solution of 40 % of the weight of solids concentration. After applying this solution to the polyimide film and drying it for 5 minutes at 140 \*\*, pressing for 70 seconds and pasting together to copper foil, after preheating for 30 seconds under  $37\text{kg/cm}^2\text{G}$  and 185 \*\* conditions -- 180 \*\* -- 4 hours (example 1) and 12 hours (example 2) -- or the cure was carried out for 24 hours (example 3), and the 90-degree peel strength (tensile strength) under room temperature conditions was measured.

[0027]In four to example 6 Examples 1-3, Epicoat 154 is \*\*\*\*\* for 5 weight sections as an epoxy resin.

[0028]In example 7 Example 2, R as a diaminopolysiloxane by the Toray Industries Dow Corning product BY16-853U[aforementioned general formula  $\text{A}_3$  ( $\text{CH}_2$ ) group,  $\text{R}_1 - \text{R}_4$  manufactured siloxane polyimide using an equivalent amount of  $\text{CH}_3$  group], and measurement of preparation of the adhesive composition using it and the 90-degree peel strength under room temperature conditions was performed.

[0029]The obtained result is shown in the next table. The value in a parenthesis is measured value about the adhesive composition which does not add a fluorochemical surfactant.

Example peel strength (kg/cm) 1 1.24 2 (0.89) 1.33 3 (0.81) 1.38 4 (0.81) 1.53 5 (0.95) 1.30 6 (0.95) 1.41 7 (0.95) 1.13 (0.93)